THE LASER AS A TOOL IN MINERAL IDENTIFICATION

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ABSTRACT

The use of a ruby laser to achieve vaporization of a microgram quantity of a mineral followed by further excitation of the vapour with an auxiliary spark source, adds a new dimension to the microanalysis of minerals by emission spectroscopy. Because the sample need not be electrically conducting, preliminary separation of the mineral from its matrix is not necessary. Areas of 50–100 microns in diameter can be examined, using polished sections or rock slices, without destruction of the specimen. The technique has been successfully applied to the qualitative identification of ore minerals in polished sections; the results obtained for silicate minerals in rock slices are less conclusive.

INTRODUCTION

The present and potential applications of the laser (or optical maser) have been much discussed in recent months with emphasis upon such fields as medicine, communications, armaments and biology, and generally upon the more spectacular of these potential uses. Its application to emission spectroscopy has received little notice until recently but, although this development is only about one year old, it is regarded as one of unusual importance.

The intense light energy from a laser is used to excite spectral emission from selected areas of the sample, such areas having a diameter of 50–100 microns. It is a two-step process; vaporization of a microgram quantity of the sample is achieved and the vapour is further excited to emit characteristic spectra of the constituent elements by means of an auxiliary spark source. The spectra are obtained independently of the electrical conductivity of the sample and thus it is possible to examine such electrically insulating materials as glass, ceramics and minerals. The name "micro-emission spectroscopy" has been coined for this new technique and the equipment is called a "laser microprobe."

The writer was afforded an opportunity to visit the laboratories of the Jarrell-Ash Company and there to use the laser microprobe to analyze qualitatively a number of polished sections of ore minerals and rock slices. This is admittedly only a preliminary study but the results suggest that micro-emission spectroscopy has much to offer to the study of geological and mineralogical specimens.

LASER THEORY

Discussion of laser theory, both simplified and in detail, has received much attention in recent months. Brief summaries are given by Lewis

(1961), Schawlow (1961), Lawrence (1963) and Levine (1963); a more detailed account will be found in the papers by Bennett (1962) and Heavens (1962) in the Supplement to *Applied Optics*, December 1962, and in a new book on the subject that has just appeared (Lengyel, 1962). It is indicative of the newness of micro-emission spectroscopy that no mention is made of it in any of these references.

Only a brief outline of the laser theory will be attempted here. A distinction should first be made between the terms "maser" and "laser." The maser (*m*olecular *a*mplification by *s*timulated *e*mission of *r*adiation) is a generic term for devices involving the amplification of electromagnetic radiation by passage of an external source of such radiation through an active medium and resulting in stimulated emission of radiation. The laser (or optical maser) is a special case of the maser in which the active medium is pumped or activated by light resulting in *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation. The laser is a new type of light source (but *not* a new type of light) in which the stimulated emission of a large number of radiating atoms is channelled into an intense light beam that is coherent, directional and nearly monochromatic.

The most popular of the solid state lasers, which were first proposed by Schawlow & Townes in 1958, is the pink ruby rod (0.05% Cr). If an intense burst of incoherent light is allowed to fall on the ruby rod, the Cr^{+++} ions are excited by the impinging light and are raised (pumped) to a higher energy level. The incoherent light is provided by an xenon flashlamp wound around, or arranged parallel to, the ruby rod. The Cr^{+++} ions, now at the higher energy level, revert to the ground state by the emission of energy in the form of red light (6944 Å). The device becomes a light amplifier when a light wave of the correct wavelength and direction of propagation travels through the active medium and is coherently amplified by stimulated emission. The device is made an oscillator by placing mirrors at each end of the rod; the stimulated radiation is made to travel back and forth between them and its intensity increases with each trip. Finally it is permitted to escape and does so as a laser pulse of brief duration and high power in the form of a burst of red light. Because the beam is nearly parallel and coherent, it can be focussed to a small spot having an extremely high power density. It is this which is used to excite the spectra of solids by vaporization of a small amount of the sample material.

EQUIPMENT

The operation of the laser microprobe is shown schematically in Fig. 1 and the details of the necessary equipment are shown in Fig. 2. It consists

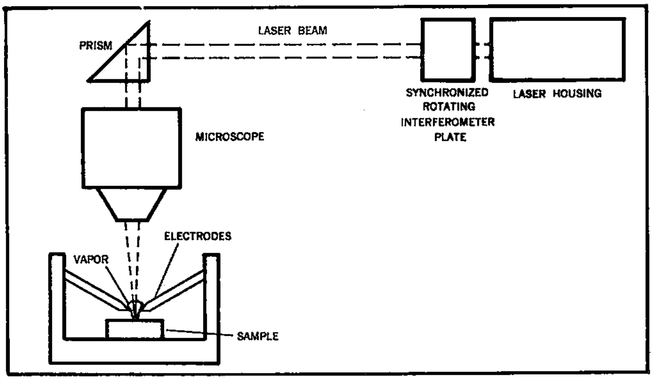

FIG. 1. Schematic representation of the operation of the laser microprobe.

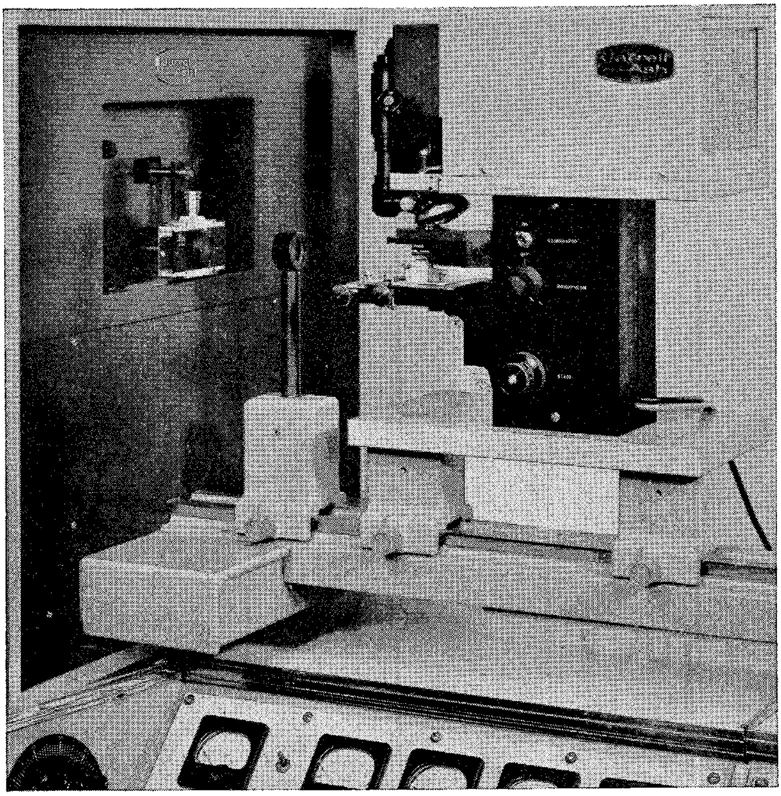

FIG. 2. The Jarrell-Ash Laser Microprobe mounted on optical bar of 3.4 metre Ebert mount spectrograph. The control console is installed below the optical bar.

of two units, the laser microprobe and the power supply. The latter, which contains the energy storage banks, triggering system and phasing control, is a unit about 4½ feet in height which fits beneath the optical bar of a spectrograph. The laser microprobe unit, weighing about 30 pounds, consists of the ruby rod surrounded by a helical xenon flashlamp, the Q-switch (an electro-optic shutter which is synchronized with the flashlamp to produce the laser pulse), a metallurgical microscope, and the auxiliary spark source consisting of a pair of 1/8″ carbon electrodes having a continuously applied potential of 1,200 volts and separated by a 3 millimetre gap, mounted between the objective lens of the microscope and the surface of the specimen. The laser microprobe can be fitted to the optical bar of any normal spectrograph. Choice of the latter is governed by the nature of the information sought but a fast spectrograph is mandatory because of the short period of light emission that is available for resolution. A single spherical lens is used to focus the light on the slit of the spectrograph.

METHOD OF OPERATION

The sample is placed upon the stage of the microscope and the area of interest is centered at the cross-hairs and brought into focus by lowering or raising the stage; the objective lens is fixed in position. The laser is fired ("lased") and the pulse is reflected down the axis of the microscope by a prism or mirror and focussed on the preselected area. The intense energy thus concentrated, estimated to be equivalent to 10,000 to 20,000° K, vaporizes a few micrograms of the material, leaving an hemispherical pit, or crater, that routinely has a diameter of about 100 microns but which can be as small as 50 microns. The vapour flashes between the auxiliary charged electrodes, ionizes the gap between them and a spark discharge occurs which excites the constituent elements of the vapour to emit characteristic spectra. The light is focussed by the spherical lens on the slit of the spectrograph. The whole process occurs in milliseconds and is accompanied by a flash of white light and a sharp report. The duration of the laser pulse is about a microsecond and the power is of the order of two or three megawatts. The laser can be fired at intervals of about one minute.

The target can be viewed after firing, although carbon deposited on the surface during the auxiliary spark discharge may obscure some details. Once a new target area has been selected, it is only necessary to insert fresh electrodes (they are contaminated by vaporized material) and recharge the capacitors before firing the laser microprobe again.

RESULTS

A series of polished sections, rock slices and one thin section were analyzed qualitatively by the method of micro-emission spectroscopy. The spectrograph used was a Jarrell-Ash, Wadsworth mount, 1.5 metre grating instrument, with a slit opening of 35 microns and a speed of *f*30. The spectra were recorded on Kodak 1030 film (35 millimetre) for the most part.

Polished ore sections and smoothed rock slices were used but such preparation is not essential except that it aids in selection of the target area, and facilitates viewing of the specimen before and after the "lasing." The allowable degree of roughness of the surface is limited by the need to maintain a suitable distance between the surface and the cross-excitation electrodes to prevent discharge of the spark to the sample surface and to keep the objective lens of the microscope from coming into contact with the laser-produced vapour. Irregularities in specimen shape can be accommodated by mounting the specimen on plasticene.

The qualitative results obtained for the ore minerals are given in Table 1. Identification was correct in each case; the presence of Mg, Ca, Si and Al in most of the samples is probably due to the occurrence of veinlets of gangue material which could not be avoided in selecting the area to be analyzed. The three shots made on the siegenite gave almost identical

TABLE 1. QUALITATIVE ANALYSIS OF ORE MINERALS BY MICRO-EMISSION SPECTROSCOPY

Mineral	Major	Minor	Trace	Faint trace
Bornite	Fe, Cu	Cr	—	Mg, Si, Ca, Ag
Sphalerite	Zn	Fe	Pb, Cd(?)	Cu, Si, Mg, Ca
Magnetite	Fe	—	Mg	Si, Mn, Ca
Sphalerite[a]	Zn	Fe	Si	Pb, Mg, Ca
Chalcopyrite[a]	Fe	Cu	—	Mg, Ca
Pyrite	Fe	Ni	—	Mg, Ca, Cu, Co, Ag
Pyrrhotite	Fe	Ni	—	Mg, Cr, Ca, Ag
Galena[b]	Pb	—	Fe, Ag	Si, Mg, Bi, Ca
Chalcopyrite[b]	Fe, Cu	Al	Cr, Mg	—
Siegenite[c]	Ni, Fe	—	Co, Mg. Cu, Zn	—
	Ni, Fe	Cu, Zn	Co, Mg	—
	Ni, Fe	Cu, Zn	Co, Mg	—
Niccolite	As	Ni	Mg, Fe	—
Skutterudite	As, Co	Ca, Fe	Ni, Cu, Cr	—
Arsenopyrite	Fe, As	Ni, Cr	Mg	—
Chromite	Fe, Cr	Ti	Mg, Al	Mn, Cu, V, Ca
Chromite	Cr	Fe, Al	Mg	—
Chromite	Fe, Cr	Al, Mn	Mg	V, Ca
Chromite	Fe, Cr	Ti, V	—	Al

[a,b] Two minerals in the same polished section.
[c] Three shots were taken.

results and, in this particular instance, served to confirm the identity of this mineral when conventional optical spectrography had failed to do so. It is interesting to note that no cross-contamination occurred when two minerals in the same section, i.e. sphalerite and chalcopyrite, galena and chalcopyrite, were lased. Additional information was obtained for some minerals in addition to their qualitative identification; the pyrite was shown to have a high Ni content, and Ag was found in a number of minerals, particularly in the galena.

The pits, or craters, were nearly hemispherical in shape and usually were formed without much visible fracturing or shattering of the specimen. A surface oxidation was visible on all specimens, as well as a deposit of carbon from the electrodes which could usually be removed by rubbing. Figs. 3–5 show the type of crater that is formed; these craters have a diameter of about 100 microns.

Laser action was not uniform for all specimens. No recognizable pits were formed in the four chromites and the area surrounding the pit in the bornite specimen showed some shattering. Thermal conductivity of the sample is believed to govern the size of the crater but such other physical properties as friability and hardness of the mineral may determine its degree of regularity. This is particularly apparent when the behaviour of silicate minerals under laser action is considered.

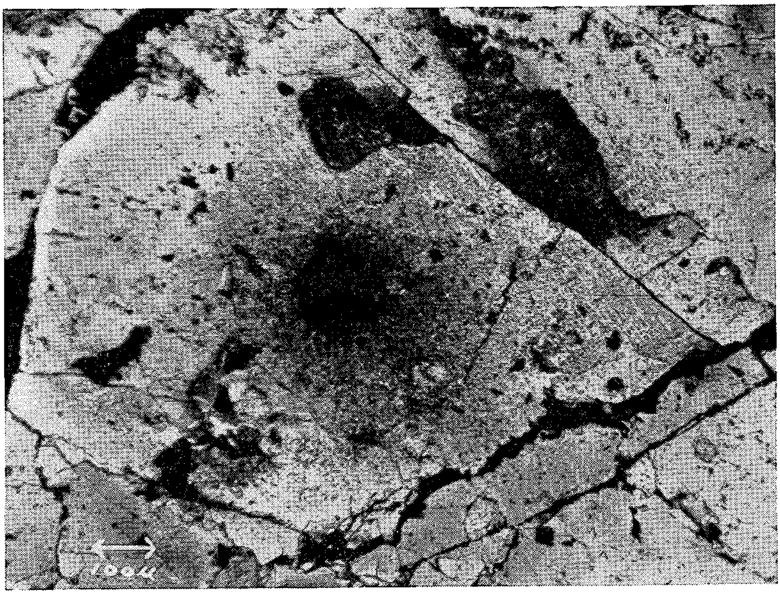

FIG. 3. Laser crater, with carbon smudge and surface tarnish, in skutterudite. Reflected light. 50×.

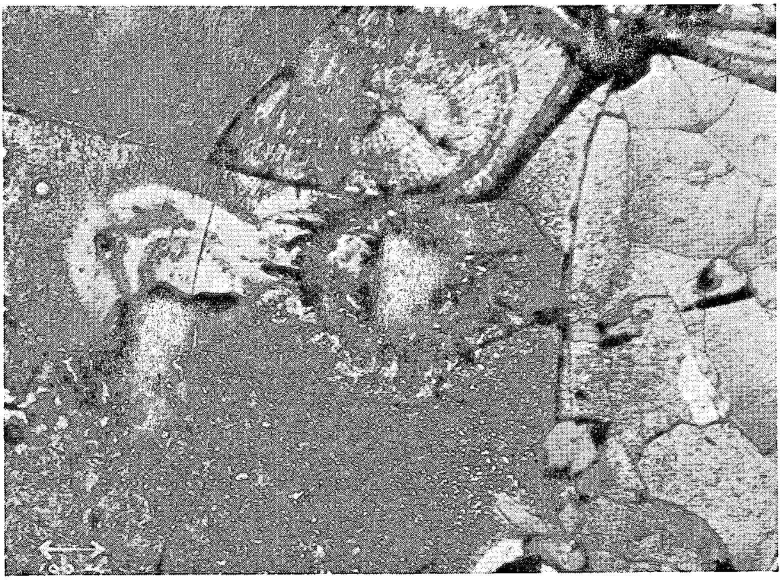

FIG. 4. Laser crater, with carbon smudge and surface tarnish, in bornite. Reflected light. 50×.

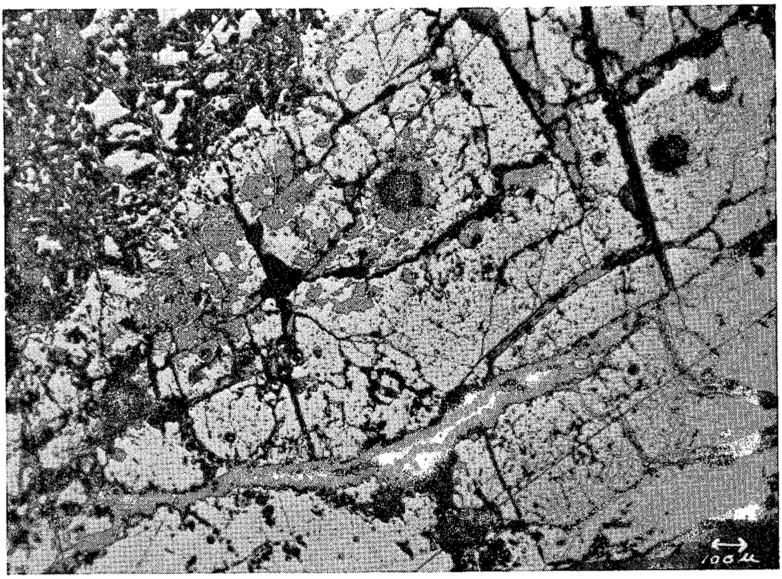

FIG. 5. Three laser craters in siegenite. Reflected light. 25×.

In Table 2 are listed the qualitative results obtained for various silicate minerals in rock slices. The results found for two of the minerals in a meteorite specimen are also included here. Zoned feldspar crystals in granite and porphyry were also examined but the spectra, recorded on Kodak 1N film instead of the 1030 film used for the other spectra, were too faint to be of any use.

TABLE 2. QUALITATIVE ANALYSIS OF SILICATE MINERALS BY MICRO-EMISSION SPECTROSCOPY

Mineral	Major	Minor	Trace	Faint trace
Clinopyroxene[a]	Si	Ca, Mg, Fe	Al	Ti
Orthopyroxene[a]	Si	Mg, Ca, Fe	Mn	Ti, Al, Cr
Orthopyroxene[a]	Si, Ca	Fe, Mg	—	Ti, Al, Cr
Plagioclase[b]	—	Mg, Ca	Si, Al	B, Fe
	—	Ca	Mg, Si, Al	B, Fe
Plagioclase[b]	—	Ca	Mg, Si, Al	B, Fe
	—	Ca	Mg, Si, Al	B, Fe
K feldspar[c]	Si, Na	K, Al	Mg, Ca	Fe
	Si, Na	K, Al	Ti, Mg, Ca	Mn, Fe
	Si, Na	K, Al	Ti, Mg, Ca	Mn, Fe
K feldspar[d]	—	Si	Ca, Mg	Al
	—	Si	Ca, Mg	Al
Kamacite[e]	Fe	Ni, Si	Cr	Mg, Ca
Enstatite[e]	Si, Ti	Mg	Fe, Al	—

[a] In pyroxenite.
[b] In anorthosite; 2 shots taken at ends of crystal.
[c] In metamorphic rock; 3 shots taken across crystal.
[d] In granophyre; 2 shots taken at edge and centre of crystal.
[e] In polished section of meteorite.

The results are not as good as those obtained for the ore minerals and the reason for this is likely to be found in one or more of the physical properties of silicates, such as thermal conductivity, brittleness, tenacity and cleavage, and the differential expansion of non-isometric minerals. The crater obtained in plagioclase feldspar, and shown in Fig. 6, is irregular but recognizable, with a fused, milky appearance. Other specimens displayed very irregular pits, with much attendant spattering of the surrounding area with fused material. Some well-shaped craters were obtained but they were exceptional. There was no problem in aiming the laser beam at a desired target; impacts could be made with ease on different zones of the same crystal.

An attempt was made to use a standard thin section, in this case one that was slightly thicker than normal (about 50 microns). The hemispherical laser pit, routinely about 100 microns in diameter, has a depth of about 50 microns and on this basis the use of a thin section with a thickness of only 30 microns is not feasible because the laser beam will burn through the slice, carbonize the cement and vaporize part of the

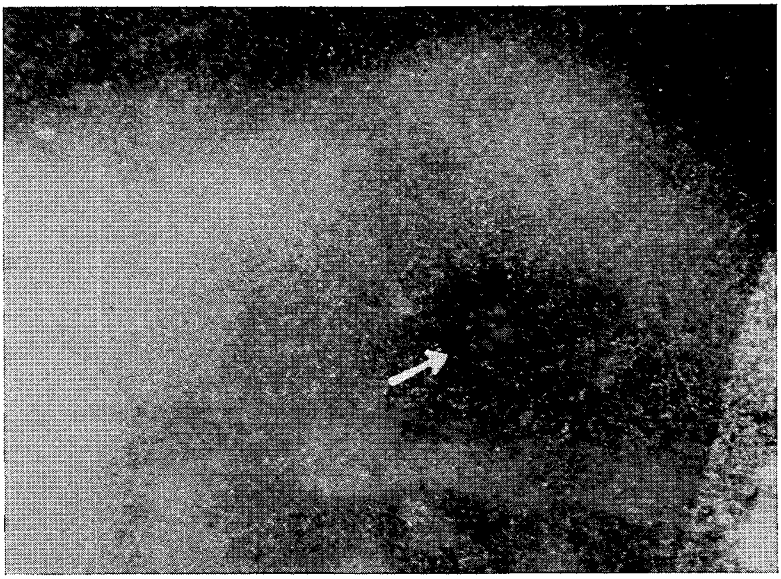

FIG. 6. Irregular laser crater (arrow) in plagioclase feldspar. Reflected light. 50×.

slide. The section consisted of magnetite-ilmenite and hercynite and both of these minerals were lased. The spectrum of the magnetite-ilmenite (the thicker of the two) showed major Ti and Al, minor Fe and Ca, and traces of Si and Mg; only major Mg, minor Fe and traces of Ca, Na and Si were found for the hercynite. The magnetite-ilmenite was much cracked and heaved, but the hercynite was blown from the slide and only a neat hemispherical crater in the glass slide indicated the position of the shot. Recent work, however, has reduced the size of the crater to 50 microns in diameter and 25 microns in depth[1] and it may yet be possible to use a standard thin section, something very much to be desired.

The routine lower limit of sensitivity obtainable with a single shot for certain elements is said to be 0.001 per cent, and the reproducibility to be ±5 per cent. The results given here are qualitative only and thus offer no opportunity to evaluate the above statements of sensitivity and precision.

CONCLUSIONS

The qualitative data given in the tables indicate that the laser microprobe can be used to identify minerals in polished sections and rock slices.

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[1] Jarrell-Ash Company; personal communication.

The results obtained in this preliminary study for the ore minerals are more satisfactory than those for the silicates but the differences in the shape of the pits produced by the laser pulse are an indication that all minerals cannot be subjected to the same treatment, as was attempted in this study. There are many variables which must be considered before progressing to semiquantitative analysis with the laser microprobe, or even before reliable qualitative results can be routinely obtained.

The effect of smoothness of the surface on laser behaviour needs to be further investigated. Is a highly polished surface more or less effective than one not so highly polished? A specimen of magnetite having an extremely high polish was lased several times and only irregular pits were formed. Was this because of the high polish or did the magnetic property or electrical conductivity of the mineral cause the spark discharge to go to the surface rather than across the electrodes?

Mention has been made of the possible effects of thermal conductivity, tenacity, brittleness, cleavage and other properties upon the nature of the crater, and upon the tendency of the mineral to shatter or fracture. Crystallographic orientation in non-isometric minerals and the nature of the bonding in crystals may also affect the magnitude of laser action.

The chief advantage of the laser microprobe over conventional arc-spark spectrography lies in the fact that the sample does not have to be electrically conducting and thus it is not necessary to remove it from its matrix in order to make it so. Another advantage is in the small amount of material (micrograms) consumed, compared with the 5 to 10 milligrams needed for conventional spectrography. This microsampling aspect of the laser has led to its being compared with the electron microprobe in application but the latter employs an electron beam of one micron or less in diameter (in comparison with which the laser becomes a macroprobe) and one can achieve much better quantitative reproducibility of results with it.

The technique of micro-emission spectroscopy with the laser microprobe is, like the laser itself, only at the threshold of its full development. Much more work is needed to determine the effects of the many factors that control the physical behaviour of minerals and further refinement of the laser microprobe itself, particularly of the ability to vary such things as the duration and intensity of the laser pulse, will doubtless be necessary. The potential usefulness of the laser microprobe as a tool for the study of geological materials will justify this work.

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